

Magnetocaloric Effect in Geometrically Frustrated Magnetic Compound HoB₁₂

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The magnetocaloric effect of frustrated antiferromagnetic HoB₁₂ is calculated. The isothermal entropy change ΔS characterising the magnetocaloric effect shows a small positive change upon magnetisation below the transition temperature T_N , indicating a small inverse magnetocaloric effect. At T_N , ΔS shows clear scaling behaviour with the applied magnetic field. The adiabatic temperature change ΔT shows paramagnetic behaviour above T_N , despite strong magnetic correlations that persist in this temperature region. The adiabatic temperature change calculated for HoB₁₂ is appreciable.

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1. Introduction

The magnetocaloric effect (MCE) in materials represents a magneto-thermodynamic phenomenon in which a change of temperature or entropy is achieved by an adiabatic or isothermal change of magnetic field [1]. As magnetic correlations limit the lowest temperature which may be achieved through magnetic cooling, paramagnetic salts have historically been used as magnetic refrigerants.

In this work we present first magnetocaloric studies of holmium dodecaboride HoB₁₂, which is a frustrated incommensurate amplitude-modulated antiferromagnet (AFM) with weak crystal field anisotropy emerging in high magnetic fields [2–4]. The paramagnetic Weiss temperature of HoB₁₂ is $\Theta_W = -24.3$ K and its Néel temperature $T_N = 7.4$ K. Neutron scattering patterns observed above T_N indicate that below $|\Theta_W|$, pronounced short range magnetic correlations appear between neighbouring Ho-ions, similar to low-dimensional magnets in a cooperative paramagnetic state [5, 6]. The magnetic entropy locked up in the spin sublattice over such a broad temperature interval is conceivably of importance to systems of this materials class and thus HoB₁₂ appears to be a very interesting and suitable candidate for magnetocaloric studies in geometrically frustrated magnetic systems.

2. Results and discussion

2.1. Isothermal entropy change

The synthesis and characterization of HoB₁₂ samples, as well as details of the measurements of which the results

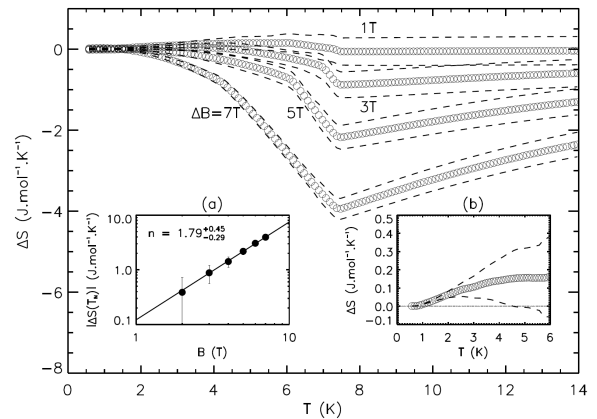


Fig. 1. The isothermal entropy change ΔS upon magnetisation calculated for HoB₁₂. Dashed lines indicate margins of error. Inset (a): $|\Delta S(T_N)|$ for various applied fields on a double-log plot to emphasize the observed power-law behaviour. Inset (b): enlargement of ΔS for $\Delta B = 1$ T showing the inverse MCE below $T = T_N$.

are analyzed in this work have been discussed elsewhere [2–4]. Shown in Fig. 1 is the isothermal entropy change upon magnetisation calculated from previously reported heat capacity data [3, 7]. Values are obtained utilising the indirect method discussed in [1]. The numerical error inherent to this method could be constrained by noting that the zero field magnetic entropy thus calculated saturates within 3% of the $R \ln 3$ value expected for HoB₁₂. The initial applied field is taken to be zero throughout, so that $\Delta B = B_f$ (B_f is the applied field which is taken as $B = \mu_0 H$ for simplicity).

Below T_N a positive value for ΔS is found for applied fields up to 5 T, which implies an inverse MCE in this

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field range, consistent with other AFM compounds [8]. The scaling behaviour of ΔS at a magnetic phase transition was recently investigated by Franco et al. [9]. In the critical region it is expected that

$$|\Delta S| \sim B^n \text{ where } n = 1 + \frac{1}{\delta} \left(1 - \frac{1}{\beta}\right). \quad (2.1)$$

Here δ and β are the critical exponents describing the dependences of the order parameter on the applied field and reduced temperature, respectively. The inset of Fig. 1 shows the absolute value of the ΔS at T_N for different applied fields. The values of $|\Delta S(T_N)|$ clearly show the expected scaling behaviour (Eq. (2.1)) with $n = 1.79^{+0.45}_{-0.29}$. Standard models of magnetism predict values of $n < 1$ [10]. For HoB_{12} $n > 1$ implies that $\Delta S/\Delta B$ increases with increasing ΔB up to at least 7 T.

2.2. Adiabatic temperature change

The calculated adiabatic temperature change ΔT upon demagnetisation is shown in Fig. 2. T_i corresponds to the temperature at which the sample is adiabatically isolated in a nonzero applied field B_i before letting $B \rightarrow 0$. Calculations presented in this section neglect the lattice contribution to the heat capacity.

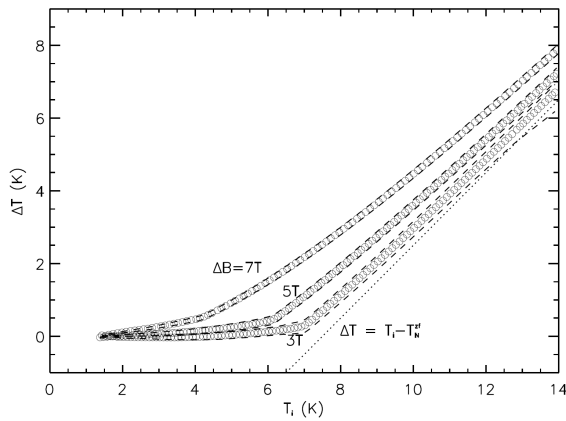


Fig. 2. The adiabatic temperature change ΔT upon demagnetisation. Dashed lines indicate margins of error. The dotted line indicates the MCE expected above a second order phase transition for $\Delta B \rightarrow 0$. T_N^{zf} is the Néel temperature in zero applied magnetic field.

Immediately above T_N , ΔT becomes linear in T_i . Despite the strong magnetic correlations that persist in this region ΔT shows paramagnetic behaviour. Below T_N a small inverse magnetocaloric effect is observed, consistent with the results for ΔS reported above. Including the entropy contribution from the lattice does not produce an MCE that differs significantly from the results shown in Fig. 2. The lattice contribution to the heat capacity is very small at $T = 14$ K (≈ 0.6 J mol $^{-1}$ K $^{-1}$. See [7]). Although not shown here, the lattice contribution does not alter the paramagnetic behaviour seen above T_N . Generally, ΔT is significantly reduced due to the lattice contribution in the region where $S(B_i, T_i) > R \ln(2J+1)$. This condition is not satisfied for $B_i \geq 3$ T and T_i up to 14 K

in HoB_{12} . The result is a large, almost paramagnetic MCE in the region above 7.4 K.

3. Conclusion

The magnetocaloric effect in HoB_{12} is calculated from heat capacity data. In the ordered region a small inverse magnetocaloric effect is observed. At T_N the isothermal entropy change shows clear scaling behaviour with applied field. The value of the exponent that describes this behaviour differs from values predicted by standard models of magnetic systems. Despite short range magnetic correlations, the behaviour of the adiabatic temperature change ΔT above T_N is asymptotically close to the behaviour expected for an ideal paramagnet, and yields appreciable changes in temperature upon adiabatic demagnetisation.

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